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Thermolysis of β-cyclodextrin/alkylcobaloxime inclusion complexes in the solid state

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Abstract

The solid state stability of a series of β-cyclodextrin/alkylcobaloxime inclusion complexes has been investigated by differential scanning calorimetery (DSC) and thermogravimetric analysis (TGA). Four distinct transitions in the TGA scans, corresponding to dehydration (Tc1), dealkylation (Tc2), breakdown of equatorial oxime ligands (Tc3), and decomposition of β-CD (Tc4) were generally seen. Three distinct transitions during DSC, corresponding to Tc1 (endotherm), Tc2 (exotherm) and Tc4 (endotherm), were observed in most cases. In addition, the temperatures of dealkylation were higher in β-cyclodextrin/alkylcobaloxime complexes than those of the corresponding alkylcobaloximes. The Tc2 changes were related to the substitution groups on the alkylcobaloximes and paralleled the stability constants of these inclusion complexes. © 1997 Elsevier Science B.V.

Keywords: Alkylcobaloxime; β-cyclodextrin; DSC; TGA; Thermal decomposition

1. Introduction

Non-covalent bonds are very important in life, for example, in enzyme–substrate interactions [1]. The host–guest complexes involving cyclodextrins (CDs), which have an interior hydrophobic cavity that can include a great variety of guest molecules [2,3], are an excellent model system for studying the nature of non-covalent bonding forces in aqueous solution [4,5]. Cyclodextrins stabilize guest molecules against, for example, heat, light, oxidizing reagents, acidic conditions [6–9].

Recently, a series of β-CD/alkylcobaloxime (β-CD/$H_2OCo(DH)_2R$, DH = bisdimethylglyoxime, R = n-C_4H_9, i-C_4H_9, n-C_5H_{11}, c-C_6H_{11}, $PhCH_2$) inclusion complexes were synthesized [10], in which alkylcobaloxime is a model for coenzyme B_{12} [11–13]. It is well known that homolysis of the Co–C bond of coenzyme B_{12} is the first key step in B_{12}-dependent enzymic reactions [14]. Studies of the non-enzymatic thermolysis of coenzyme B_{12} at evaluated temperatures suggest that the B_{12}-dependent enzymes are capable of catalyzing the homolysis of the Co–C bond by some 9–12 orders of magnitude [15,16]. While details of the mechanism by which these enzymes achieve this level of catalysis remain obscure, there

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is general agreement that the flexibility of the corrin ring is important and that enzymes exploit this property by inducing an upward flex in the corrin ring to sterically accelerate Co–C bond cleavage [17]. It is necessary to investigate the characters of the Co–C bond after formation of β-CD/alkylcobaloximes inclusion complexes and to compare them with those of the alkylcobaloximes. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are useful techniques in the study of host–guest inclusion complexes involving CDs [6,7] as well as alkylcobalt complexes [18,19] in the solid state. This study investigates the stability of alkylcobaloximes, β-CD, and β-CD/alkylcobaloxime complexes.

2. Experimental

Alkylcobaloximes were synthesized by standard reductive alkylation methods [20]. β-CD/alkylcobaloxime inclusion complexes were obtained [10]: $H_2OCo(DH)_2R$ and β-CD, in their 1 : 1 molar ratio, were dissolved in water at 50°C. The resulting solution was filtered and the filtrate was stored at 25°C in the dark. Within one week, red-brown crystals precipitated. The product was filtered and washed with water.

TGA experiments were performed on a Perkin–Elmer 7 Series Thermal Analysis system. The flow rate of nitrogen was about 80 ml/min. Samples (4–5 mg) were held in an open platinum boat. A heating rate of 10°C min^{-1} was employed.

For DSC, a Perkin–Elmer DSC-2C thermal analyser was used. Sample weights were about 2–4 mg. Sealed aluminium pans were used. Nitrogen was used as a purge gas and a heating rate of 10°C min^{-1} was employed.

3. Results and discussion

TGA and DSC scans for $H_2OCo(DH)_2n\text{-}C_5H_{11}$, β-CD, β-CD/$H_2OCo(DH)_2n\text{-}C_5H_{11}$ are shown in Figs. 1 and 2 respectively. First derivative curves of TG (DTG) are also shown. The data are summarized in Tables 1 and 2 respectively. The characteristic temperatures were taken as the peak temperatures in the TG scans and the peak temperatures of the endotherms or exotherms in the DSC scans.

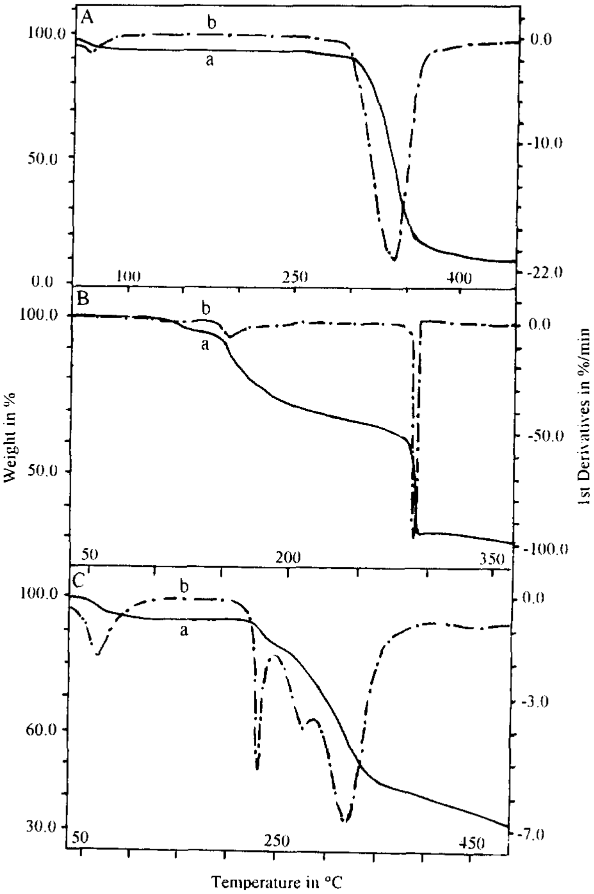

Fig. 1. (a) Thermogravimetric analysis (TGA) and (b) first derivative curves of TG scans of (A) β-CD (B)$H_2OCo(DH)_2n\text{-}C_5H_{11}$ and (C) β-CD/$H_2OCo(DH)_2n\text{-}C_5H_{11}$.

According to the studies of Brown et al. [18], the thermal decomposition of $H_2OCo(DH)_2R$ includes three transitions. The first transition corresponds to the loss of axial water, which was coordinated to the cobalt atom (T1), the next transition was due to loss of the axial organic ligand (T2) and the final transition was attributed to the decomposition of the equatorial ligand (T3). Three transitions were obvious in the TG study on $H_2OCo(DH)_2n\text{-}C_4H_9$ and $H_2OCo(DH)_2n\text{-}C_5H_{11}$. However, for $H_2OCo(DH)_2i\text{-}C_4H_9$ and $H_2OCo(DH)_2c\text{-}C_6H_{11}$, the T1 and T2 transitions overlapped and for $H_2OCo(DH)_2PhCH_2$, all three transitions (T1, T2, T3) overlapped. For the last three

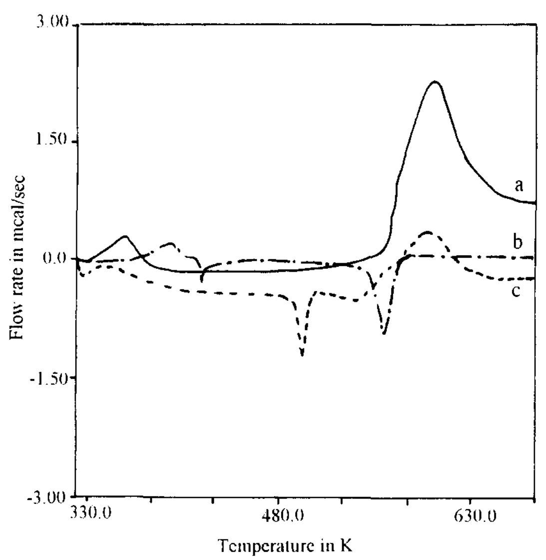

Fig. 2. DSC scans for (a) β-CD (b) $H_2OCo(DH)_2n\text{-}C_5H_{11}$ and (c) β-CD/$H_2OCo(DH)_2n\text{-}C_5H_{11}$

compounds, their T1 and T2 events could not be separated by derivative TG. Moreover, it was observed that the values of weight loss were acceptably consistent with those calculated on the basis of their molecular formula. The T3 transition, which should be the same for all compounds as it involves only the common 'core' complexes (bis(dimethylglyoximato) cobalt(II)), occurred at virtually the same temperature for each complex (around 280°C) [18]. Additionally, the values of the characteristic temperatures for the various transitions agreed well between the two techniques. The enthalpy associated with the thermal decomposition of (bis(dimethylglyoximato)cobalt(II)) was fairly constant for each alkylcobaloxime. Finally, T2, the dealkylation temperatures, decreased as the size of the R group increased; that is, $n\text{-}C_4H_9 > i\text{-}C_4H_9 > n\text{-}C_5H_{11} > c\text{-}C_6H_{11}$. These results are consistent with those of Brown et al. [18].

There were only two gradually changing transitions in the TG scans of β-CD/$H_2OCo(DH)_2R$; one transition ranged from room temperature to about 150°C, the other from 150°C to about 500°C. However, three weight loss steps were observed in the second transitions of the derivative TG scans of the inclusion complexes, where $R{=}n\text{-}C_4H_9$, $i\text{-}C_4H_9$, $n\text{-}C_5H_{11}$ and $c\text{-}C_6H_{11}$. Comparing the TG scans of the complexes with those of β-CD and the corresponding $H_2OCo(DH)_2R$, the first transitions (Tc1), the processes of the weight loss of the axial water ligand in $H_2OCo(DH)_2R$ and of water in crystal structure, overlapped. In the second transitions, there were three steps corresponding to the loss of R groups in alkylcobaloximes (Tc2), the decomposition of bisdimethylglyoxime ligands (Tc3) and the final decomposition of β-CD (Tc4). However, in both TG and derivative scans, the Tc3 transition for β-CD/$H_2OCo(DH)_2PhCH_2$ was not obvious.

These assignments are supported by several observations. Firstly, the weight losses accompanying the Tc1 transitions were in agreement with those calculated for the loss of both axial water and water associated with the crystal structures. Secondly, the axial alkyl ligand loss temperatures (Tc2) of β-CD/$H_2OCo(DH)_2R$ were higher than those of the corresponding alkylcobaloximes. The differences were about 45°C ($R{=}i\text{-}C_4H_9$), 47°C ($R{=}c\text{-}C_6H_{11}$, 50°C ($R{=}n\text{-}C_4H_9$) and 79°C ($R{=}n\text{-}C_5H_{11}$) respectively. In addition, the dealkylation temperatures in β-CD/$H_2OCo(DH)_2R$ increased in the order: $c\text{-}C_6H_{11} < i\text{-}C_4H_9 < n\text{-}C_4H_9 < n\text{-}C_5H_{11} < PhCH_2$. This was different from that for $H_2OCo(DH)_2R$ mentioned above. The proposed structure of β-CD/$H_2OCo(DH)_2R$ was that the R groups were included into the cavity of β-CD and the plane involving the Co atom and bis(dimethylglyoximato) was placed near the wide opening of β-CD [10,21,22]. After the R groups were included into the β-CD cavity, there were hydrophobic and Van der Waals interactions between the β-CD cavity and alkyl groups, as well as hydrogen bonds between β-CD and dimethylglyoximato [21,22]. These interactions would give additional restrictions to the thermal mobility of the alkyl groups relative to the plane involving the cobalt atom and bis(dimethylglyoximato), and stabilized the cobaloximes. Therefore, the temperatures of cleavage of the Co–C bond in cobaloxime were probably related to the extent of inclusion of the alkyl groups into the CD cavity as well as the association constants of the inclusion complexes. According to our investigation [21], the formation constants (at 25°C in D_2O) of $R{=}PhCH_2$ and $n\text{-}C_5H_{11}$ ($10^4\,M^{-1}$) are much bigger than those of $R{=}i\text{-}C_4H_9$, $n\text{-}C_4H_9$ and $c\text{-}C_6H_{11}$ (10^2–$10^3\,M^{-1}$). These data probably explain the fact that the Tc2 of $R{=}PhCH_2$ (264°C) and $n\text{-}C_5H_{11}$ (232°C) were higher

Table 1
Weight loss, temperature of peak and temperature range of weight loss for $H_2OCo(DH)_2R$ and β-CD/$H_2OCo(DH)_2R$ in TGA scans

Complex	Substance *: water in crystal structure	Weight loss (%) values in ( ) are calculated from the molecular formula	Peak temperature (°C)	Temperature range of weight loss (°C)
$H_2OCo(DH)_2i\text{-}C_4H_9$	H_2O, $i\text{-}C_4H_9$	23.7 (20.6)	155	40–205
	DH	70.6 (63.3)	277	205–325
β-CD/$H_2OCo(DH)_2i\text{-}C_4H_9\cdot 13H_2O$	H_2O^*	13.5 (13.3)	64	40–113
	H_2O	1.0 (1.3)	120	113–143
	$i\text{-}C_4H_9$	3.0 (3.3)	200	143–214
	DH	15.3 (13.3)	280	214–289
	β-CD		320	
$H_2OCo(DH)_2n\text{-}C_4H_9\cdot H_2O$	H_2O^*, H_2O	9.1 (9.4)	116	640–143
	$n\text{-}C_4H_9$	17.2 (15.0)	171	143–192
	DH	58.5 (60.2)	273	192–350
β-CD/$H_2OCo(DH)_2n\text{-}C_4H_9\cdot 4H_2O$	H_2O^*, H_2O	6.0 (5.7)	70	40–150
	$n\text{-}C_4H_9$	6.8 (3.6)	221	150–242
	DH	13.9(14.7)	279	242–289
	β-CD		320	
$H_2OCo(DH)_2n\text{-}C_5H_{11}$	H_2O	5.4 (4.7)	117	40–173
	$n\text{-}C_5H_{11}$	19.5 (18.8)	153	173–184
	DH	45.1 (60.9)	290	184–350
β-CD/$H_2OCo(DH)_2n\text{-}C_5H_{11}\cdot 2H_2O$	H_2O^*, H_2O	6.3 (3.5)	66	40–162
	$n\text{-}C_5H_{11}$	7.5 (4.6)	232	162–249
	DH	14.6 (14.9)	277	249–290
	β-CD		322	
$H_2OCo(DH)_2$ $c\text{-}C_6H_{11}$	H_2O, $c\text{-}C_6H_{11}$	27.8 (25.9)	144	40–184
	DH	60.7 (59.0)	280	184–325
β-CD/$H_2OCo(DH)_2c\text{-}C_6H_{11}.8H_2O$	H_2O^*	9.0 (8.6)	83	40–102
	H_2O	2.3 (1.1)	118	102–157
	$c\text{-}C_6H_{11}$	6.3 (5.0)	191	157–244
	DH	13.8 (13.8)	280	244–286
	β-CD		320	
$H_2OCo(DH)_2PhCH_2$	H_2O, $PhCH_2$, DH		299	
β-CD/$H_2OCo(DH)_2PhCH_2\cdot H_2O$	H_2O^*, H_2O	9.1 (9.2)	84	40–160
	$PhCH_2$		264	
	β-CD		322	

than those of R=$i\text{-}C_4H_9$ (200°C), $n\text{-}C_4H_9$(221°C) and $c\text{-}C_6H_{11}$ (191°C).

Thirdly, the Tc3 for all inclusion complexes and the T3 of the individual alkylcobaloximes were at ~280°C. In the structure of β-CD/$H_2OCo(DH)_2R$, the R group is included into CD cavity, and the equatorial plane $Co(DH)_2$ is near the opening of CD. Therefore, after the loss of axial alkyl ligands, the 'core' complexes should be common for β-CD/$H_2OCo(DH)_2R$ and $H_2OCo(DH)_2R$. Tc3 and T3 all correspond to the temperatures for decomposition of bis(dimethylglyoximato) cobalt(II).

Finally, the temperatures of final decomposition (Tc4) did not obviously change for each β-CD/$H_2OCo(DH)_2R$ complex being about 320°C and similar to that of decomposition temperature of β-CD itself (340°C). The differences might be due to the conformation change of β-CD after formation of host–guest inclusion complexes [2].

In the DSC scans of β-CD/$H_2OCo(DH)_2R$ complexes, there were only three transitions corresponding to the Tc1, Tc2, Tc4 transitions observed during TG. The Tc1 and Tc4 transitions were endothermic and the Tc2 transitions were exothermic. The Tc3 transition (exothermic) was overlapped by the Tc4 transition. DSC data for β-CD/$H_2OCo(DH)_2R$ and $H_2OCo(DH)_2R$ are shown in Table 2. The characteristic temperatures, for example, the Tc2 in the DSC

Table 2
Temperature and enthalpies for $H_2OCo(DH)_2R$ and β-CD/$H_2OCo(DH)_2R$ in DSC

Complex	Substance *: water in crystal structure	Temperature (°C)	Enthalpies (kJ mol^{-1})
β-CD	H_2O	87	2.2
	β-CD	330	1.5×10^3
$H_2OCo(DH)_2i\text{-}C_4H_9$	H_2O	137	2.5
	i-C_4H_9	145	−1.8
	DH	284	-1.1×10^2
β-CD/$H_2OCo(DH)_2i\text{-}C_4H_9\cdot13H_2O$	H_2O *, H_2O	89	2.91
	i-C_4H_9	193	−3.1
	DH, β-CD	321	5.1×10^2
$H_2OCo(DH)_2n\text{-}C_4H_9\cdot H_2O$	H_2O,H_2O	139	3.23
	n-C_4H_9	165	−3.5
	DH	286	-1.0×10^2
β-CD/$H_2OCo(DH)_2n\text{-}C_4H_9\cdot4H_2O$	H_2O *, H_2O	83	2.64
	n-C_4H_9	213	−4.6
	DH, β-CD	321	6.2×10^2
$H_2OCo(DH)_2$ n-C_5H_{11}	H_2O	121	3.2
	n-C_5H_{11}	147	−5.5
	DH	287	-1.1×10^2
β-CD/$H_2OCo(DH)_2n\text{-}C_5H_{11}\cdot2H_2O$	H_2O *, H_2O	57	1.4
	n-C_5H_{11}	226	−5.6
	DH, β-CD	321	6.6×10^2
β-CD/$H_2OCo(DH)_2c\text{-}C_6H_{11}\cdot8H_2O$	H_2O *, H_2O	88	6.2
	c-C_6H_{11}	186	−1.5
	DH,β-CD	321	6.69×10^2
$H_2OCo(DH)_2PhCH_2$	H_2O	124	3.1
	$PhCH_2$	156	−3.5
	DH	296	-1.0×10^2
β-CD/$H_2OCo(DH)_2PhCH_2$.H2O	H_2O, H_2O	88	2.0
	$PhCH_2$	257	−9.0
	DH, β-CD	321	5.4×10^2

scans, were in general agreement with those seen with TG. The enthalpies associated with the final decomposition of bisdimethylglyoximatecobalt(II) and β-CD were similar for all inclusion complexes ($5.1\sim6.7\times10^2$ kJ mol^{-1}), but were much smaller than that of decomposition of β-CD itself (1.5×10^3 kJ mol^{-1}). This is due, firstly to the breakdown of the 'core' complex being exothermic while the decomposition of β-CD being endothermic and secondly to there probably being some conformation changes for β-CD after the R groups were included into the cavity.

4. Conclusion

The overall pattern of the degradation of β-CD/$H_2OCo(DH)_2R$ was loss of water, followed by dealkylation, 'core' complex breakdown and finally decomposition of β-CD. The dealkylation temperatures measured by TG and DSC of the inclusion complexes were about 191°C and 186°C(R = c-C_6H_{11}), 200°C and 193°C (R = i-C_4H_9), 221°C and 213°C (R = n-C_4H_9), 232°C and 226°C(R = n-C_5H_{11}), 264°C and 257°C (R = $PhCH_2$) respectively. Comparisons between the dealkylation temperatures and those of corresponding guest molecules revealed that the Co–C bond was much more stable after the R groups had been included into the β-CD cavity.

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